IV.C.1c NIST Center for Neutron Research in Support of the Hydrogen Sorption Center of Excellence

Dan Neumann (Primary Contact),
Craig M. Brown, Yun Liu, Jae-Hyuk Her
National Institute of Standards and Technology (NIST)
NIST Center for Neutron Research
MS 8562
100 Bureau Dr.
Gaithersburg, MD 20899
Phone: (301) 975-5252; Fax: (301) 921-9847
E-mail: dan@nist.gov

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

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Objectives

- Quantify the amount, location, bonding states and dynamics of hydrogen in hydrogen sorption materials.
- Direct partner synthesis efforts based on the understanding gained through the use of scattering techniques.
- Demonstrate the fundamental characteristics of useful hydrogen storage materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

NIST provides important materials metrologies for Center partners using neutron-scattering measurements to understand and characterize hydrogen-substrate interactions of interest to the Center.

Enhanced Hydrogen Storage using Metal-Organic Frameworks (MOFs):

This project is conducting fundamental studies of how hydrogen binds in MOFs with exposed metal sites. Insights gained from these studies will be used by Center partners and applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: $4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Determined bulk elemental compositions of materials of interest to the Center. These include metal decorated carbon-based materials, MOFs, and boron-infused carbon materials. This understanding helps to speed sample development and material synthesis aimed at reaching the DOE goals of specific energy (2 kWh/kg) and energy density (1.5 kWh/L).
- Determined the location of hydrogen binding in several crystalline materials. Provides atomistic understanding of how hydrogen is adsorbed.
- Illustrated the site-specific hydrogen adsorption strength in MOF materials. The overall appreciation of this determines the isosteric heats of hydrogen adsorption.
- Proved that hydrogen can be adsorbed in a layer that is denser than that in solid hydrogen. Provided a potential mechanism for development of new materials that can achieve DOE gravimetric targets. A minimum surface area of ≈1,400 m^2/g is needed to achieve 6 wt% hydrogen storage capacity.

Introduction

To obtain the DOE levels of hydrogen storage in a timely manner, it is imperative that trial-and-error testing of materials be avoided. Thus, the focus must be upon the rational design of new systems. From a thorough understanding of the physics and chemistry that governs the hydrogen-substrate interactions, we will be able to make a more concerted effort to push the frontiers of new materials. The key to improving materials is a detailed understanding of the atomic scale locations of the hydrogen and determining how it gets there and how

it gets out. Neutron scattering is perhaps the premier technique for studying hydrogen and the NIST Center for Neutron Research is currently the leading facility in the U.S. for studying these materials.

Approach

NIST provides important materials characterization for Center partners using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of hydrogen in carbon-based materials such as polymers, MOFs, and carbonaceous materials such as carbon nanohorns. NIST works directly with Center partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine and resolve the fundamental issues that need to be addressed.

Results

Enhanced Physisorption

NIST and the National Renewable Energy Laboratory co-lead Research Cluster 3. The Cluster is to understand hydrogen interactions with metal ions and focuses on the rational synthesis of sorbents that can strongly bind multiple di-hydrogen ligands. Di-hydrogen ligands may be bound to a single metal atom with binding energies in a desirable range for vehicular hydrogen storage. The synthesis of materials that have open, isolated metal sites exhibiting moderate H_2 binding energies, with interactions potentially similar to those observed in Kubas-type complexes, will be explored and optimized by the appropriate Cluster members. Key issues are balancing the reactivity of the hydrogen sorption sites with their stability and hydrogen capacity given a 2 bar delivery pressure.

MOFs exhibiting stronger binding interactions are needed to facilitate H_2 adsorption at higher temperatures, and, indeed, a binding energy of 15 kJ/mol has been predicted to maximize the amount of adsorbed H_2 accessible at 298 K and up to 20 bar [1]. We have previously used neutron powder diffraction to demonstrate that the highest (at the time) observed maximum isosteric heat of adsorption (10.1 kJ/mol) observed for a MOF was directly related to H_2 binding at coordinatively unsaturated Mn^{2+} centers within a framework [2]. This observation also held for other MOFs with coordinatively unsaturated metal centers (CUMC) of different metal ions [3-4]. While these efforts have made significant progress, the low surface packing density (SPD) of many carbon materials at technically relevant temperatures has limited their adsorption capabilities. For example, if H_2 in MOF-177, (surface area ≈4,500 m^2/g)[5], had a similar hydrogen surface density to that of hydrogen in activated carbons, its excess adsorption would reach ≈ 9.0 wt% rather than 7.5 wt% at 77 K.

A collaborative Center study of MOF-74 [6] (with C. C. Ahn, California Institute of Technology), using neutron powder diffraction alongside isotherm measurements, show that H_2 adsorbed on the MOF-74 surface has a higher surface density at 77 K than that of solid H_2 at ≈4 K and zero pressure. Our results reveal the shortest intermolecular D_2-D_2 distance observed in a physisorption-based material without the application of pressure (Figure 1). We can attribute part of this high density to the presence of coordinatively unsaturated Zn^{2+} centers that promote intermolecular deuterium distances of about 2.85 Å at 4 K. This observation, along with results from other systems with CUMCs that exhibit large SPDs, presents an avenue to increase the surface density of adsorbed hydrogen in this class of materials [7] (Figure 2).

In order to understand how an attractive surface potential decreases the H_2-H_2 distance and to determine if sorbent-sorbate interactions can significantly increase the SPD beyond that in MOF-74, we performed quantum mechanical calculations on a model system. The combined results of experiment and calculation seem to indicate that the adsorption potentials for a hydrogen molecule in framework structures are large enough to induce a high SPD at 77 K. The SPD of 4.3×10-5 g/m^2

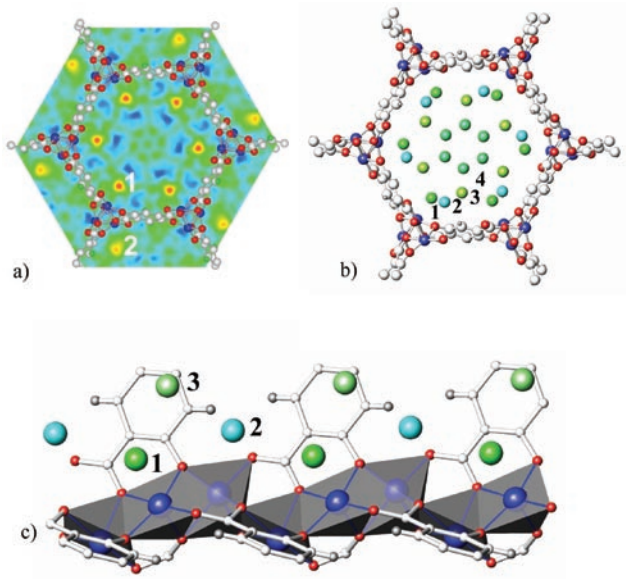

FIGURE 1. D_2 Adsorption Sites in MOF-74 at a Loading of 4.2 D_2:Zn – a) Suppositions of Fourier difference map together with the crystal structure of MOF-74 projected down the *c*-axis. The red-yellow regions indicate the high scattering regions of the first two adsorption sites. b) The four D_2 adsorption sites identified by neutron powder diffraction (labeled 1-4, spheres of green and light blue). c) The first three D_2 adsorption sites are shown with the first site directly interacting with the Zn^{2+} ions (blue balls) at a distance of 2.6 Å.

calculated from our model system is roughly the upper limit for the SPD of a physisorption system, which in turn sets a minimum surface area required for a working material based on surface physisorption methods. Our estimate indicates a minimum surface area requirement of ≈1,400 m^2/g (or ≈2,100 m^2/g) for a material that can reach an excess adsorption of 6 wt% (or 9 wt%) [7].

Engineered Nanospace

Although the crystal structures of MOFs are typically composed of rigid frameworks, they can demonstrate significant structural distortions upon adsorption/desorption of guest molecules. An extreme aspect of this type of distortion occurs as a "breathing" effect that is typically associated with a large change of the internal pore volume. MIL-53, which is made up of corner-sharing metal (Cr or Al) clusters interconnected with benzenedicarboxylate organic ligands [8], has also shown reversible structural changes due to the framework interaction with guest molecules. Upon removal of solvent molecules by evacuating the sample at moderate temperatures, MIL-53 has an open structure with a large internal volume. However, at room temperature, it adsorbs water, significantly reducing the volume of the unit cell by shrinking the pores. There is some speculation in the literature that such a breathing mechanism may be useful for hydrogen storage applications. We have initiated studies (in collaboration with General Motors Corporation) aimed at evaluating the applicability of this mechanism to achieving the hydrogen storage goals of Research Cluster 1.

Our work shows that MIL-53(Al) can be converted to a closed-pore phase by only decreasing temperature and without the aid of any guest molecules. A very large hysteresis as a function of temperature exists. The transition from the open-pore phase to the closed-pore phase is observed between 125 K and 150 K, while the transition from the closed-pore phase to open-pore phase occurs between 325 K and 375 K. An important impact of this is that we cannot know, *a priori,* the structural composition of a bare material without the knowledge of its thermal history (Figure 3). This becomes especially important for gas adsorption isotherm experiments using the volumetric method, where one usually has to measure the empty volume of a sample, which is typically obtained at room temperature with low-pressure helium gas. In order to correctly relate the empty volume information to the correct structure of MIL-53(Al), we have to clearly understand its thermal history and relate that to the phase diagram that has the potential to be different for each synthesized material and also dependant on heating/cooling rates.

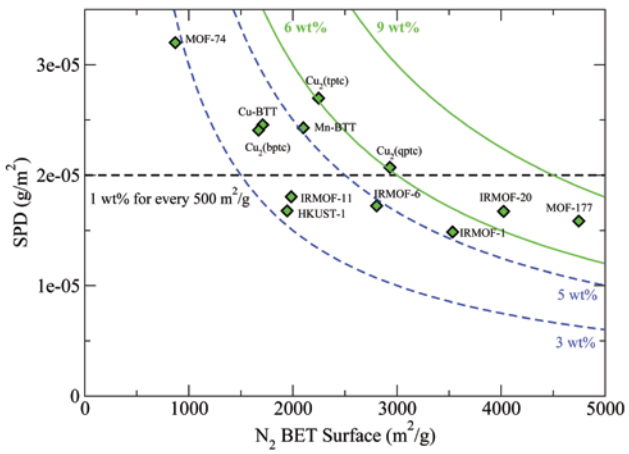

FIGURE 2. The H_2 Surface Packing Density, SPD, as a Function of N_2 Brunauer-Emmett-Teller (BET) Surface Area – The MOFs with CUMCs, in general, show larger SPD compared to those without CUMCs. The horizontal dashed line shows the SPD for typical carbon material where every 500 m^2/g of N_2 BET surface area can adsorb 1 wt% of H_2. Solid green curves show the lines for gravimetric uptake of 6 wt% and 9 wt%.

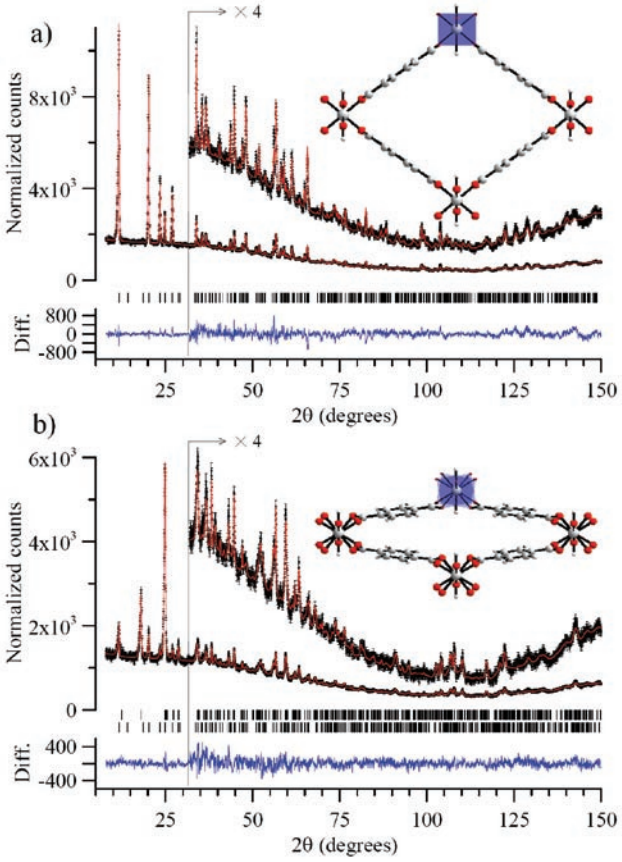

FIGURE 3. Neutron powder diffraction data (black points) of MIL-53(Al) collected at room temperature after heating to 450 K (upper) and cooling to 77 K (lower). MIL-53(Al) exists either as an open-pore phase or a predominantly closed-pore phase, depending on the thermal history. The solid red lines are Rietveld refinement fits to the data using the structural models illustrated in the insets. Vertical markers give Bragg peak positions for the respective phases and the solid line beneath is the difference between the experimental and calculated intensities with the same vertical scale. Note the scaling factor applied to the upper patterns and the difference data for angles greater than 26°.

The combined effects of the structural transitions together with our observed slow transition rate significantly affect volumetric gas adsorption measurements and can be used to explain the previously published steps and hysteresis in the hydrogen isotherm data. Additional work is underway to understand the structural transitions upon hydrogen adsorption and in evaluating the 'breathing' of the framework as a potential hydrogen storage mechanism.

Doped Materials

NIST has contributed to the efforts of Research Cluster 2 using non-destructive bulk elemental determination from prompt-gamma activation analysis (PGAA) of Center synthesized samples. The results of the PGAA has steered synthetic approaches of the Pennsylvania State University team aimed at optimizing the boron contents of both microporous boron-substituted carbons (Mike Chung) and nano-porous carbons with and without boron (Hank Foley and Ramakrishnan Rajagopalan). Additional small-angle neutron scattering and inelastic neutron scattering (INS) measurements on nano-porous carbons have been used to gain insights into the morphology of the pore structure and how hydrogen is adsorbed into these materials.

Hindered hydrogen rotational spectra in the INS are observed at low loadings suggest that hydrogen molecules are first adsorbed in the predominant 1 nm sized nano-pores. The INS peak character changes between at hydrogen loadings between 0.8 wt% and 1.6 wt% and may indicate that hydrogen molecules continue to be adsorbed in larger pores with lower curvature of the graphitic walls resulting in a much smaller barrier to hydrogen rotation.

Conclusions and Future Directions

The main conclusions of this years work can be summarized as follows:

- Determined that open metal centers in MOF materials not only enhance the enthalpy for hydrogen adsorption, but also improve the density at which hydrogen is adsorbed in the monolayer.
- A minimum surface area of 2,100 m^2/g is estimated for a material that can reach a gravimetric target of 9 wt%.
- Determined the temperature dependence of the structural transition in a flexible framework material, MIL-53.
- The hysteresis and slow transformation kinetics of the MIL-53 transition significantly affect volumetric gas adsorption measurements.

To determine a set of optimized characteristics for hydrogen sorption in MOFs with CUMCs, more measurements of fundamental parameters are needed. We will study structures and hydrogen interactions in MOFs with different metal centers, ligands, anionic frameworks, and pore geometries. We will spend some effort to attempt to understand how hydrogen is adsorbed in the flexible framework MIL-53. This may shed light on if it is possible to use the framework flexibility in a beneficial way for increasing the working temperature of these materials. Potential mechanisms can be kinetic hindering of hydrogen desorption or having a hydrogen 'clamp' depending on the openness of the pores. We will continue to aid the other Center partners in characterizing their materials aiming to understand the fundamental characteristics that improve hydrogen storage capabilities.

Special Recognitions & Awards/Patents Issued

1. Yun Liu: winner of the 2008 Sigma-Xi NIST Chapter Postdoctoral Poster Prize.

FY 2008 Publications/Presentations

1. Increasing the density of adsorbed hydrogen with coordinatively unsaturated metal centers in metal-organic frameworks, Y. Liu, H. Kabbour, C.M. Brown, D.A. Neumann, and C.C. Ahn, Langmuir, 2008, 24, 4772.

2. Observation of CuII-H^2 interactions in a fully-desolvated, sodalite-type metal-organic frameworks, M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann and J.R. Long, Angewandte Chemie, 2007, 46, 1419.

3. Inelastic neutron scattering of H_2 adsorbed in HKUST-1, Y. Liu, C.M. Brown, D.A. Neumann, V.K. Peterson, and C. Kepert, J. Alloys Compounds, 2007, 446, 385.

4. Inelastic neutron scattering of H_2 adsorbed on boron substituted single walled carbon nanotubes, Y. Liu, C.M. Brown, J.L. Blackburn, D.A. Neumann, T. Gennett, L. Simpson, P. Parilla, A.C. Dillon and M.J. Heben, J. Alloys Compounds, 2007, 446, 368.

5. Neutron Powder Diffraction of Metal-Organic Frameworks for Hydrogen Storage, C.M. Brown, Y. Liu and D.A. Neumann, PRAMANA Physics Journal (2008).

6. Hydrogen Adsorption in MOF-74 Studied by Inelastic Neutron Scattering, Y. Liu, C.M. Brown, D.A. Neumann, H. Kabbour, and C.C. Ahn, in Life Cycle Analysis for New Energy Conversion and Storage Systems, edited by V.M. Fthenakis, A.C. Dillon, and N. Savage (Mater. Res. Soc. Symp. Proc. Volume 1041E, Warrendale, PA, 2007), 1040-R2_03.

7. Applications of Neutron Scattering Techniques to Hydrogen Storage Materials, Y. Liu, C.M. Brown, T.F. Baumann, D.A. Neumann, proceedings of the American Nuclear Society Annual Meeting, December 2007.

8. Structural Characterization of D2 in Cu_3(1,3,5-benzenetricarboxylate)$_2$ using Neutron Powder Diffraction, V.K. Peterson, Y. Liu, C.M. Brown, C.J. Kepert, 6th Pacific Rim International Conference on Materials and Processing and published in Materials Science Forum Vols. 561-565 pp.1601, (2007).

9. Inelastic Neutron Scattering As A Probe Of The States Of Hydrogen In Carbon Materials, C. M. Brown, Y. Liu, H. Hu, S. Rols, A.A. Puretzky, B. Zhou, C.M. Rouleau, D. Styers-Barnett, D.A. Neumann, D.B. Geohegan. Carbon 2007 Proceedings, Seattle.

10. Tailoring Of Single Walled Carbon Nanohorns For Hydrogen Storage And Catalyst Supports, H. Hu, B. Zhao, A.A. Puretsky, C.M. Rouleau, D. Styers-Barnett, D.B. Geohegan, C.M. Brown, Y. Liu, W. Zhou, H. Kabbour, D.A. Neumann, C. Ahn. Carbon 2007 Proceedings, Seattle.

11. Synthesis of Microporous Boron-Substituted Carbon (B/C) Materials Using Polymeric Precursors for Hydrogen Physisorption, T. C. M. Chung, Y. Jeong, Q. Chen, A. Kleinhammes, and Y. Wu, J. American Chem. Soc., 2008, 130, 6668.

Presentation

1. C.M. Brown, "Impact of coordinatively unsaturated metal sites on hydrogen affinity and surface packing density", American Chemical Society Spring Meeting, New Orleans Apr. 6th-10th, 2008.

2. C.M. Brown, "Enhancing the interaction strength and capacities of hydrogen storage via surface adsorption", American Physical Society March Meeting, New Orleans Mar. 9th-14th, 2008. Invited

3. C.M. Brown, "Impact of coordinatively unsaturated metal sites on hydrogen affinity and surface packing density", International Symposium on Neutron Scattering, Mumbai, India, Jan. 15th-18th, 2008. Invited

4. C.M. Brown, "Inelastic neutron scattering as a probe of the states of hydrogen in carbon materials", Carbon 2007, Seattle. W.A., July 15th 2007. Keynote address.

5. Y. Liu, "Investigating Dihydrogen Binding to Coordinatively Unsaturated Metal Centers in Metal-organic Frameworks", American Conference on Neutron Scattering, 2008, Santa Fe, NM, May 2008.

6. Y. Liu, "Hydrogen Storage in Metal-Organic Frameworks", Canadian Neutron Beam Centre, Ontario, Canada, Apr. 2008. Invited

7. Y. Liu, "Improving Hydrogen Storage in Metal-organic Frameworks Using Exposed Metal Sites", Department of Physics & Astronomy, McMaster University, Canada, Apr. 2008. Invited

8. Y. Liu, "Reversible Structural Transition of MIL-53 and its Effect on Hydrogen Storage Materials", Material Research Society, 2008 Spring Meeting, San Francisco, CA, Mar. 2008.

9. Y. Liu, "Improving Hydrogen Storage in Metal-organic Frameworks Using Exposed Metal Sites", Department of Materials Science and Engineering, Uni. Of Pennsylvania, Feb. 2008. Invited

10. Y. Liu, "Storing H2 in Nano-porous Materials", Materials Science Division, Argonne National Laboratory, Argonne, IL, Dec. 2007. Invited

11. Y. Liu, "Hydrogen Storage in Nano-porous Materials", NIST Center for Neutron Research, Gaithersburg, MD, Dec. 2007.

12. Y. Liu, "Impact of Coordinatively Unsaturated Metal Sites of MOFs on H2 Affinity and Surface Packing Density", Material Research Society, 2007 Fall Meeting, Boston, MA, Nov. 2007. Invited

13. Y. Liu, "Improving the Packing Density of Adsorbed Hydrogen and a Novel Configuration of Hydrogen Molecules in MOF-74", Material Research Society, 2007 Fall Meeting, Boston, MA, Nov. 2007.

14. Y. Liu, "Application of Neutron Scattering Techniques to Hydrogen Storage Materials", ANS/ENS International Meeting and Nuclear Technology Expo, Washington, D.C., Nov. 2007. Invited

15. D.A. Neumann, "Hydrogen storage ad neutron scattering at NIST", Erlangen, Germany, May 2007.

16. D.A. Neumann, "Hydrogen storage ad neutron scattering at NIST", TU Munich, Germany, May 2007.

17. D. Neumann, "Hydrogen storage and neutron scattering at NIST", Carnegie-Mellon University, PA, Nov. 2007.

18. J.-H. Her, "Temperature dependent Structural Changes of MIL-53, A potential H_2 Storage Material", American Conference on Neutron Scattering, 2008, Santa Fe, NM, May 2008.

19. J.-H. Her, "Temperature and Gas type/Pressure dependent Structural Changes of MIL-53, A potential H_2 Storage Material", American Crystallographic Association, 2008, Knoxville, TN, June 2008.

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3. M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann and J.R. Long, *Angewandte Chemie Int. Ed*., **2007**, 46,1419.

4. V.K. Peterson, Y. Liu, C.M. Brown and C. Kepert, *J. Am. Chem. Soc*., **2006**, 128, 15578.

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7. Y. Liu, H. Kabbour, C.M. Brown, D.A. Neumann, and C.C. Ahn, *Langmuir*, **2008**, 24, 4772.

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